Development of biomarker proxies for terrestrial methane cycling

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Our understanding of past methane (CH_4) cycle dynamics is limited and there are no proxy methods to reconstruct ancient CH_4 concentrations beyond the reach of the Antarctic ice cores (< 800 kyr). Previous studies suggest that the carbon isotopic composition ($\delta^{13}C$) of bacterial geohopanoids can be used to infer relative changes in wetland CH_4 cycling. However, the environmental controls regulating the carbon isotopic composition of hopanoids in modern wetland settings remains poorly constrained. Here we undertake an unprecedented global survey of hopanoid $\delta^{13}C$ values in a range of peat-forming environments (n = >100 samples from 13 globally widespread sites), spanning a wide temperature (~5 to 28°C) and pH (~3 to 8) range.

In our global compilation, hopanoid distributions are dominated by the C_{32} ββ hopanoic acid and the C_{31} αβ hopane. The latter has been attributed to rapid isomeric catalysation at the C-17 position as a result of acidic conditions. Our global compilation is consistent with this hypothesis, with more αβ geohopanoids in acidic peats. Our results also indicate a statistically significant correlation ($p < 0.05$) between hopane $\delta^{13}C$ values and mean annual air temperature. In temperate peatlands, the $\delta^{13}C$ value of C_{31} hopanes range from -22 to -26‰ and do not capture a strong methanotroph signal. This is consistent with recent work that suggests heterotrophic organisms are the dominant hopanoid producers in peat. In tropical peatlands, C_{31} hopanes are increasingly ^{13}C-depleted, ranging between -30 to -32‰. Increasing ^{13}C-depletion with increasing temperature can be attributed to either: 1) enhanced methanogenesis and therefore greater methane oxidation and/or 2) enhanced respiration and greater utilisation of recycled CO_2 by photoautotrophs.

Our results also provide evidence for incorporation of methane or recycled CO_2 into peat-forming plants, via ^{13}C-depletion of mid-chain *n*-alkanes (relative to long-chain *n*-alkanes). The occurrence of *Sphagnum*-associated methanotrophy was previously observed in living moss species. However, this is the first evidence that this signal is preserved in the sedimentary record and could provide a complementary tool for tracing wetland methane cycling.